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Synthesis and structural characteristics of Hg-Ba-Ca-Cu-O high temperature superconductor

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Abstract The $HgBa_2CaCu_2O_{6+\delta}$ (Hg 1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg 1223) phases of Hg-Ba-Ca-Cu-O system have been synthesised, with same starting nominal compositions $Ha_{1.1}Ba_{2.1}Ca_2Cu_3O_z$ at ambient pressure, employing single step direct oxides route. The X-ray diffraction (XRD) and transmission electron microscopic (TEM) investigations revealed that the material sintered at 720°C for 6 h contained dominantly tetragonal Hg 1212 phase with lattice parameters $a = b = 3.86$ Å and $c = 12.76$ Å, whereas materials sintered at 750°C for 8h contained dominantly tetragonal Hg 1223 phase with lattice parameters $a = b = 3.86$ Å and $c = 15.87$ Å. The $R - T$ measurements of the as – synthesised materials showed transition temperatures in the range of 90 – 110K. In this paper, details of synthesis parameters and structural – microstructural features of the as – synthesised materials have been described and discussed.

Keywords Synthesis, structural – microstructural characteristics, high temperature superconductivity

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1. Introduction

The discovery of superconductivity above 130 K in Hg-Ba-Ca-Cu-O high temperature superconducting (HTSC) system has initiated intensive study on the mercury based compounds [1-3]. Particularly so, since the superconducting transition temperature (T_c) and the irreversibility line of HTSC phases of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1, 2, 3,$---) are higher than those of $Bi_2Sr_2CaCu_2O_8$ (Bi : 2212) most commonly used for the development of large – scale applications. Furthermore, the observations of higher T_c onsets in multiphase samples of Hg-Ba-Ca-Cu-O system, suggest that an increase in T_c may be expected for single phase samples, once the doping levels are optimized. Although, the synthesis of HTSC phases of Hg-Ba-Ca-Cu-O system has been carried out by several workers [3-5], the effects of processing parameters relating to heating rate, sintering temperature and duration, and cooling rate which influence the final phase formation crucially have not been established rigorously, particularly for the single step direct oxides route [6]. Keeping this in view, the present investigations on synthesis of Hg: 1212 and 1223 phases have been carried out to explore and study the effect of the above described processing parameters on the formation of HTSC phases of the Hg bearing cuprate high temperature superconductors. The structural – microstructural characteristics of the as synthesized samples have been explored through X-ray diffraction and electron microscopic techniques. Special attempts have been made to explore microstructural characteristics such as presence of stacking faults, inter-growth structures and possible occurrence of higher members ($n > 3$) of the HTSC phases in the as – synthesized Hg bearing HTSC materials.

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2. Experimental

To synthesise the HTSC phases of Hg-Ba-Ca-Cu-O system, first appropriate amounts of HgO, BaO, CaO and CuO were mixed and ground thoroughly in a closed glove box having P_2O_5, NaOH and Ar/ N_2 atmosphere. After grinding, the resulting mixture was pelletized at a pressure of 3-5 ton / inch^2. The pellets were closed inside a silver box. The silver box containing the pellets was sealed inside a silica tube evacuated to 10^{-2} torr. The sealed tube was closed inside a steel container to avoid possible explosion due to high vapour pressure of Hg at high temperature. The steel container was kept inside a programmable Heraeus furnace. In the present work, samples were synthesised by

adopting several final sintering temperatures *e.g.* 700, 720, 730, 740, 750 and 760°C and also several time spans *e.g.* 4, 5, 6, 7, 8, 9 and 10 hours. The heating rate upto 600°C was kept about 200°C/h to avoid the formation of the insulating $CaHgO_2$ phase. Thereafter, it was kept between 100 to 150 °C/h upto final sintering temperature.

The phase identification of the as-synthesised samples was carried out by employing PW 1710 Philips diffractometer fitted with a graphite monochromator and using Cu-Kα radiation. The transition temperatures of the samples were measured by using standard four probe method employing van der Pauw geometry. Microstructural features of the as synthesised samples were studied with the help of a computerised Philips electron microscope (EM CM-12).

3. Results and discussion

The as-synthesised samples of the Hg – bearing cuprate superconductors were subjected to X-ray diffraction for gross structural characterisation. Figure 1 shows a representative X-ray diffraction pattern of the samples sintered at 720 °C for ~ 6h and cooled at the rate of 50 °C/h. The analysis of this pattern revealed the presence of dominantly tetragonal phase with $a = b = 3.87$ Å and $c = 12.76$ Å, this corresponds to the lattice structure of Hg : 1212 phase. Figure 2 shows XRD pattern of the sample sintered at 750 °C for ~ 8 h and cooled at the rate of 50 °C/h. Analysis of this pattern revealed the presence of tetragonal phase with $a = b = 3.86$ Å and $c = 15.87$ Å, corresponding to Hg : 1223 phase. In addition to this, some diffraction peaks were also indexed with Hg : 1212 phases. The indexing of the peaks corresponding to these phases (Hg : 1212 and 1223) has been depicted in the figure.

The variation of electrical resistance with temperature of the as-synthesised samples of Hg-bearing cuprate superconductors was measured by standard four-probe method employing the van der Pauw geometry. A representative R-T curve of the sample sintered at 750 °C for ~ 6 h and cooled at the rate of 50 °C/h has been shown in Figure 3.

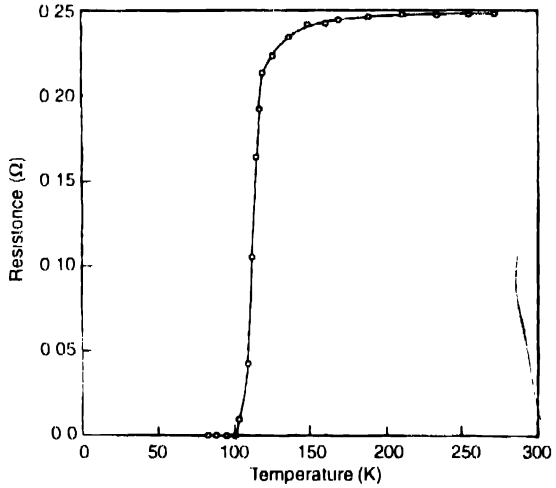


Figure 3. Resistance *vs* temperature curve of HTSC sample synthesised with nominal composition $Hg_{1.2}Ba_{1.8}Ca_2Cu_3O_x$ and sintered at ~ 720°C for ~ 6 h.

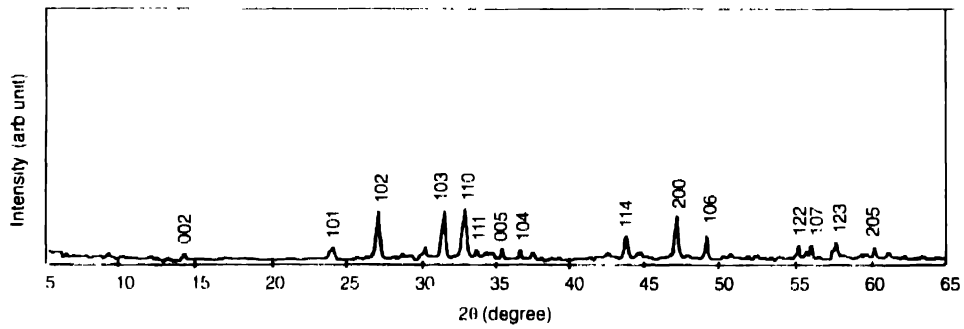


Figure 1. X-ray diffraction pattern of Hg-Ba-Ca-Cu-O HTSC system sintered at ~ 720°C for ~ 6 h, showing the presence of dominantly $HgBa_2CaCu_2O_{6+\delta}$ HTSC phase.

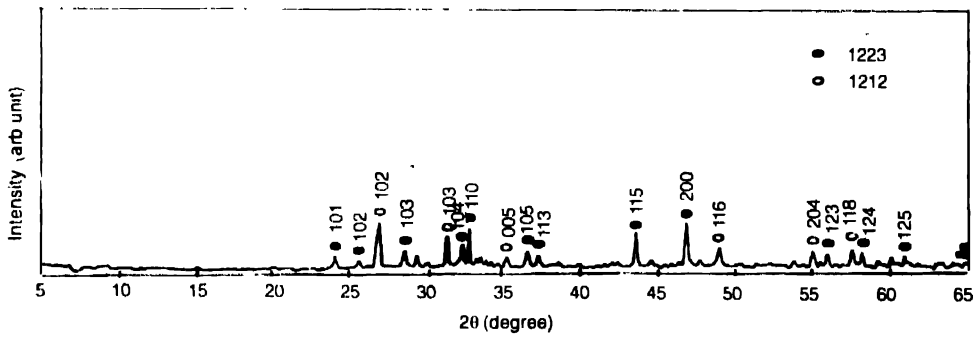
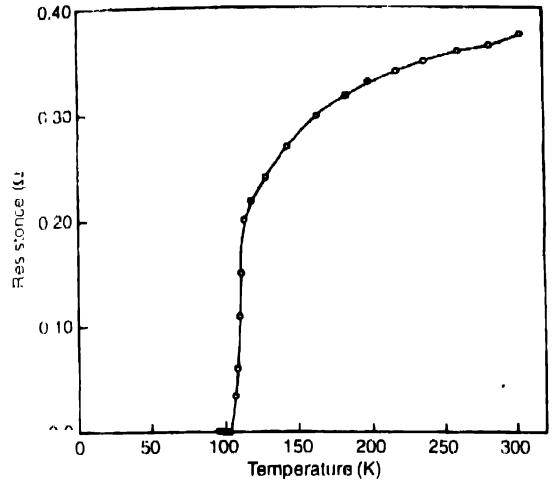


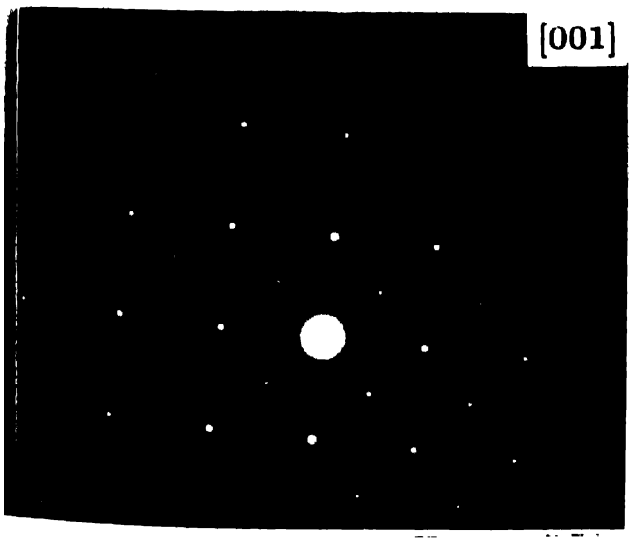
Figure 2. X-ray diffraction pattern of Hg-Ba-Ca-Cu-O HTSC system sintered at ~ 750°C for ~ 8 h, showing the presence of dominantly $HgBa_2Ca_2Cu_3O_{8+\delta}$ HTSC phase. Peaks corresponding to Hg-1223 and 1212 phases have been marked by • and o respectively.

The curve shows superconducting onset at ~ 120 K and T_c ($R = 0$) ~ 100 K. Another representative R–T curve of the samples ntered at 750°C for ~ 8 h and cooled at the rate of 50 °C/h hibiting superconducting onset at ~ 130 K and T_c ($R = O$) ~ 105 has been shown in Figure 4.



gure 4. Resistance vs temperature curve of HTSC sample synthesised h nominal composition $Hg_1Ba_2Ca_2Cu_3O_x$ and sintered at ~ 750°C for s h

The microstructural features of the as-synthesised samples re explored by employing transmission electron microscopic chnique (TEM). In the present investigations, TEM plorations spread over several specimens of well-tested mples (through XRD and R-T measurements) of Hg bearing iprate superconductors. Based on the TEM studies it has been und that basic crystal structure of as-synthesised samples rrespond to tetragonal Hg : 1212 and 1223 as substantiated XRD studies also. Figure 5 shows a representative selected ea electron diffraction (SAD) pattern, bringing out a^*–b^* ciprocal lattice net. The analysis of this pattern revealed the esence of tetragonal structure with $a = b = 3.86$ Å. Figure 6 ows [010] SAD pattern taken from the specimens of the sample



gure 5. [001] SAD pattern of Hg-Ba-Ca-Cu-O HTSC system, showing agonal phase with $a = b = 3.86$ Å.

sintered at 750 °C for ~ 6 h and cooled at the rate of 50 °C/h. This figure correspond to tetragonal Hg : 1212 phase with $a = 3.87$ Å and $c = 12.76$ Å. A representative SAD pattern bringing out a^*–c^* reciprocal lattice net taken from the sample sintered at 750°C

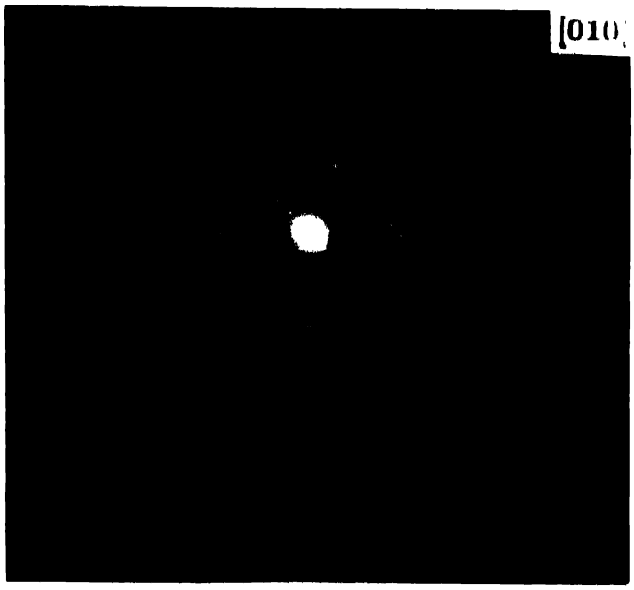


Figure 6. SAD pattern exhibiting the presence of $HgBa_2Ca_2Cu_3O_{8+\delta}$ HTSC phase ($a = 3.87$Å, $c = 12.76$ Å)

for ~ 8 h and cooled at the rate of 50 °C/h and exhibiting tetragonal Hg : 1223 type phase with $a = 3.86$ Å and $c = 15.86$ Å, has been shown in Figure 7. These TEM results are in conformity with XRD results. In the present work, TEM explorations of several samples of the Hg-Ba-Ca-Cu-O system did not reveal the presence of any modulated structure or stacking faults. This result is in sharp contrast with the case of Bi and Tl – bearing cuprates

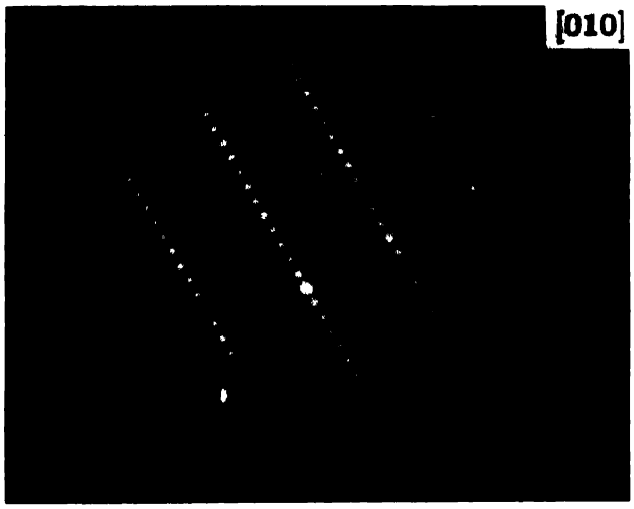


Figure 7. SAD pattern exhibiting the presence of $HgBa_2Ca_2Cu_3O_{8+\delta}$ HTSC phase ($a = 3.86$ Å, $c = 15.86$ Å).

Based on the extensive investigations in the present work, the optimum synthesis parameters *i.e.* heating rate, sintering temperature / duration and cooling rates, for synthesis of nearly

single phase materials of Hg : 1212 and 1223 are summarised in the Table 1.

Table 1. Optimum synthesis parameters

Phase	
HG : 1212 (a=b=3.87 Å, c=12.76 Å)	**Hg : 1223** (a=b=3.86 Å, c=15.86 Å)
Heating rate : (a) 200°C/h upto 600°C (b) 100–150°C/h after 600°C	**Heating rate :** (a) 200°C/h upto 600°C (b) 100–150° C/h after 600°C
Final sintering temp./time : 720°C/6 h	**Final sintering temp./time :** 750°C/8h
Cooling rate : 50°C/h	**Cooling rate :** 50°C/h

The XRD and TEM explorations revealed the synthesis of nearly single phase Hg : 1212 and 1223 phase in the present work by employing single step direct oxide route. However, the superconducting transition temperatures (T_cs) were not as high as those reported by other workers [5, 7]. In the present case, it is thought that as-synthesised HTSC phases are oxygen deficient and hence underdoped (*i.e.* carrier density in the CuO_2 layer is less than the optimum value). The carrier density in the CuO_2 layer can be optimised (with enhancement in T_c) by annealing the sample in O_2 atmosphere or partially substituting suitable cations of higher valence than Hg^{2+} at Hg site. Since the Hg containing compounds are very sensitive to moisture and CO_2 present in the atmosphere. It is not convenient to anneal the samples in O_2 atmosphere for a long time to introduce extra oxygen in the HgO layer and hence optimise the carrier density in order to achieve the highest T_c. During heating and cooling, there is a possibility of carbon atoms getting trapped in the structure which may destroy the superconducting property of the material. The second method can be used by taking the samples in evacuated sealed silica tube. This method is being adopted to stabilise and improve the superconducting transition temperatures of Hg : 1212 and 1223 samples [8,9].

4. Conclusions

In the present investigation, we have synthesised the HTS phases (Hg : 1212 and 1223) of Hg-Ba-Ca-Cu-O through a sing step direct oxides synthesis route. The T_cs of the as-synthesise samples have been found to be in the range of 90 – 110K. A interesting result emanating out of the present studies relat to the fact that unlike the case of other cuprate HTSC phas (*e.g.* Bi and Tl bearing cuprates), for the Hg : 1212 and 1223, t as-synthesised materials prepared on the present formati processes, correspond to nearly single phase materials free fr any mixed or defect (*e.g.* stacking faults) phases.

Acknowledgments

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